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Quality Assurance

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Introduction

Quality assurance (QA) is a system of activities and processes put in place to ensure that monitoring and measurement data meet user requirements and needs. Quality control (QC) consists of procedures used to verify that prescribed standards of performance in the monitoring and measurement process are met. Department of Energy (DOE) orders and guidance mandate QA requirements for environmental monitoring of DOE facilities. DOE Order 5400.1 identifies QA requirements for radiological effluent and surveillance monitoring and specifies that a QA program consistent with the DOE order addressing quality assurance is established. This order sets forth policy, requirements, and responsibilities for the establishment and maintenance of plans and actions that assure quality in DOE programs.

LLNL conducted QA activities in 1998 at the Livermore site and Site 300 in accordance with the *Environmental Protection Department Quality Assurance Management Plan*, (Revision 3), based on DOE Order 5700.6C which prescribes a risk-based, graded approach to QA. This process promotes the selective application of QA and management controls based on the risk associated with each activity, maximizing effectiveness and efficiency in resource use.

The DOE *Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance* (U.S. Department of Energy 1991) requires that an environmental monitoring plan be prepared. LLNL environmental monitoring is conducted according to procedures published in Appendix B of the LLNL *Environmental Monitoring Plan* (Tate et al. 1995). LLNL or commercial laboratories analyze environmental monitoring samples using Environmental Protection Agency (EPA) standard methods, when available. When EPA standard methods are not available, custom analytical procedures, usually developed at LLNL, are used. The radiochemical methods used by LLNL laboratories are described in procedures unique to the laboratory performing the analyses. LLNL uses only State-of-California-certified laboratories to analyze its environmental monitoring samples. In addition, LLNL requires all analytical laboratories to maintain adequate QA programs and documentation of methods.

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Quality Assurance Activities

Nonconformance reporting and tracking is an LLNL quality assurance process aimed at ensuring that Environmental Protection Department (EPD) activities meet the department's QA requirements and that problems are found, identified, resolved, and prevented from recurring. LLNL generated 92 Nonconformance Reports (NCRs) related to environmental monitoring in 1998 compared to 87 in 1997 and 106 in 1996.

Thirty-one of the 92 NCRs generated in 1998 were due to problems with analytical laboratories, and 26 were due to errors in documentation, training, or procedures. Minor problems with sewer monitoring equipment accounted for another 18 NCRs, 11 were related to air-monitoring equipment, and the remaining 6 were related to other monitoring networks.

LLNL addresses analytical laboratory problems with the appropriate laboratory as they arise. Many of the NCRs that were written in response to problems with the laboratories concern minor documentation or paperwork errors, which were corrected soon after they were identified. Other problems—such as missed holding times, late analytical results, and typographical errors on data reports—accounted for the remaining NCRs related to the analytical laboratories. The majority of these were corrected by reanalysis, resampling, reissued reports, or corrected paperwork, and associated sample results were not affected.

LLNL addresses internal documentation, training, and procedural errors by conducting formal and informal training. These errors generally do not result in lost samples but may require extra work on the part of sampling and data management personnel to resolve or compensate for the errors.

Analytical Laboratories

In March 1996, LLNL and Lawrence Berkeley National Laboratory entered into three-year Blanket Service Agreements (BSAs) with six off-site analytical laboratories (Harrach et al. 1998). In 1998, LLNL began a bidding process for future analytical laboratory work because those BSAs were scheduled to end in March 1999. As part of the rebid process, LLNL developed requirements for a statement of work, solicited and reviewed bids from laboratories, audited the laboratories, and reviewed their performance on evaluation samples. LLNL took the number and frequency of past NCRs with laboratories currently providing analytical services for LLNL into account when reviewing bids.

New BSAs were signed with seven analytical laboratories in March 1999; of these seven, four are continuing service and three are serving the Laboratory for the first time. LLNL is working closely with its new and continuing analytical laboratories to minimize the occurrence of problems in the future.

Participation in Laboratory Intercomparison Studies

The LLNL Chemistry and Materials Science Environmental Services (CES) Environmental Monitoring Radiation Laboratory (EMRL) and the Hazards Control Department's Analytical Laboratory (HCAL) participated in both the annual EPA Environmental Monitoring Systems Laboratory (EMSL) intercomparison studies program and the annual DOE Environmental Monitoring Laboratory (EML) intercomparison studies program. A review of the EMSL study indicates that 29 of 31 analyses reported by CES and 13 of 14 analyses reported by HCAL fell within established acceptance control limits. For the EML studies, 66 of 73 reported by CES and 10 of 10 results reported by HCAL fell within the established acceptance control limits.

CES EMRL participated in a DOE Mixed Analyte Performance Evaluation Program (MAPEP) study in 1998. Eleven of 11 analytes reported by CES fell within acceptable limits. (Samples for a second 1998 MAPEP study were distributed in January 1999 so results will be reported in the *Environmental Report 1999*.)

HCAL also participated in four EPA Water Pollution and Water Supply intercomparison studies for metals during 1998. Review of these results shows that values for 24 of 24 samples fell within established acceptance control limits.

Both CES and HCAL have implemented changes that are intended to address the root causes of unacceptable intercomparison study results and prevent future results from falling outside the acceptance control limits.

Details of the intercomparison study results, including the follow-up explanation and response for data that fell outside the acceptance control limits, are presented in the Data Supplement. Although contract laboratories are also required to participate in laboratory intercomparison programs, permission to publish their results for comparison purposes was not granted for 1998.

LLNL uses the results of intercomparison program data to identify and monitor trends in performance and to solicit corrective action responses for unacceptable results. If a laboratory has unacceptable performance for a particular test in two consecutive

performance evaluation studies, LLNL may chose to select another laboratory to perform the affected analyses until the original laboratory can demonstrate that the problem has been corrected. Continued unacceptable performance or failure to prepare and implement acceptable corrective action responses could result in formal notification of unsatisfactory performance by the LLNL Procurement Department (for off-site contract laboratories). If the problem still cannot be corrected, termination of the BSA with contract laboratories or suspension of use of the on-site laboratory could result.

A joint performance evaluation committee composed of members from EPD, CES, and Lawrence Berkeley National Laboratory is creating a systematic process for evaluating laboratory performance using performance evaluation samples. A method for evaluating the results of intercomparison studies will be developed by that committee.

Duplicate Analyses

Duplicate or collocated samples are distinct samples of the same matrix collected as closely to the same point in space and time as possible and are intended to be identical in all respects. Collocated samples processed and analyzed *by the same organization* provide intralaboratory information about the precision of the entire measurement system, including sample acquisition, homogeneity, handling, shipping, storage, preparation, and analysis. Collocated samples processed and *analyzed by different organizations* provide interlaboratory information about the precision of the entire measurement system (U.S. Environmental Protection Agency 1987). Collocated samples may also be used to identify errors—for example, mislabeled samples and data entry errors.

Tables 14-1 through **14-3** present statistical data for collocated sample pairs, grouped by sample matrix and analyte. Samples from both the Livermore site and Site 300 are included. **Tables 14-1** and **14-2** contain data pairs in which both values are detections (see Statistical Methods in this chapter). **Table 14-3** contains data pairs in which either or both values are nondetections.

Precision is measured by the percent relative standard deviation (%RSD); see the EPA *Data Quality Objectives for Remedial Response Activities: Development Process*, Section 4.6 (U.S. Environmental Protection Agency 1987). Acceptable values for %RSD vary greatly with matrix, analyte, and analytical method; however, lower values represent better precision. The results for %RSD given in **Table 14-1** are the 75th percentile of the individual precision values.

Table 14-1. Quality assurance duplicate sampling. Summary statistics for analytes with more than eight pairs in which both results were above the detection limit.

Media	Analyte	N[a]	%RSD[b]	Slope	r^2[c]	Intercept
Air	Beryllium[d]	13	18.4	0.439	0.53	4.90 (pg/m^3)
	Gross beta	94	21.4	1.04	0.91	1.55×10^{-8} (Bq/L)
	Uranium-235 by mass	12	3.27	1.10	0.96	-3.88×10^{-7} (μg/m^3)
	Uranium-238 by mass	12	3.56	1.09	0.96	-4.80×10^{-5} (μg/m^3)
	Tritium (air)[e]	30	32.3	1.67	1.0	–0.0513 (Bq/L)
Radiation dose	90-day radiation dose	29	2.48	1.02	0.96	–0.248 (mrem)
Ground water	Arsenic	21	6.73	1.00	1.0	-3.65×10^{-5} (mg/L)
	Barium	13	2.32	0.992	1.0	0.00149 (mg/L)
	Chromium[e]	13	10.3	0.867	0.55	0.00129 (mg/L)
	Copper	9	8.44	0.916	0.99	6.26×10^{-5} (mg/L)
	Gross alpha	17	25.4	0.941	0.82	0.0219 (Bq/L)
	Gross beta[e]	19	31.7	0.818	0.026	0.174 (Bq/L)
	Nitrate (as NO_3)	20	1.91	1.08	0.98	–3.35 (mg/L)
	Potassium	23	5.66	0.941	0.99	0.168 (mg/L)
	TDS[f]	9	1.54	0.946	0.99	42.0 (mg/L)
	Tritium	10	2.01	0.989	1.0	3.65 (Bq/L)
	Uranium-233+234[e]	19	30.3	0.848	0.43	0.0289 (Bq/L)
	Uranium-238	19	25.4	0.896	0.91	0.00744 (Bq/L)
	Vanadium	9	3.89	0.957	0.97	0.00201 (mg/L)
	pH	9	0.538	1.03	0.98	–0.234 (pH units)
Sewer	Gross alpha[d]	14	41.6	0.439	0.057	0.121 (Bq/L)
	Gross beta	48	6.78	1.04	0.99	–0.0324 (BqL)

a Number of duplicate pairs included in regression analysis.

b 75th percentile of percent relative standard deviation (%RSD) where $\%RSD = \left(\frac{200}{\sqrt{2}}\right)\left(\frac{|x_1 - x_2|}{x_1 + x_2}\right)$ and x_1 and x_2 are the reported concentrations of each routine-duplicate pair.

c Coefficient of determination.

d Outside acceptable range of slope or r^2 due to variability.

e Outside acceptable range of slope or r^2 due to outliers.

f TDS = Total dissolved solids.

Table 14-2. Quality assurance duplicate sampling. Summary statistics for selected analytes with eight or fewer pairs in which both results were above the detection limit.

Media	Analyte	N[a]	Mean ratio	Minimum ratio	Maximum ratio
Air	Gross alpha	3	0.99	0.87	1.1
	Plutonium-238[b]	2	0.64	0.32	0.96
Ground water	Radium-226[b]	7	1.4	1.2	2.1
	Radium-228	5	0.87	0.071	1.3
	Trichloroethene	6	0.91	0.81	1.0
	Uranium-235+236[b]	7	1.6	0.34	3.7
Rain	Tritium	1	1.1	1.1	1.1
Runoff (from rain)	Gross alpha	4	1.1	0.61	1.8
	Gross beta	2	1.2	0.91	1.5
	Tritium	2	0.95	0.90	0.99
Soil	Beryllium	2	1.3	1.1	1.5
	Cesium-137	4	1.3	0.90	1.8
	Plutonium-239+240[b]	3	2.0	1.1	3.7
Sewer	Tritium	5	0.99	0.93	1.0
Vegetation	Tritium	5	0.94	0.59	1.1

a Number of data pairs.

b Outside acceptable range of 0.7–1.3, for mean ratio.

Regression analysis consists of fitting a straight line to the collocated sample pairs. Good agreement is indicated when the data lie close to a line with slope equal to one and intercept equal to zero, as illustrated in **Figure 14-1**. Allowing for normal analytical variation, the slope of the fitted line should be between 0.7 and 1.3, and the absolute value of the intercept should be less than the detection limit. The coefficient of determination (r^2) should be >0.8. These criteria apply to pairs in which both results are above the detection limit.

If there were more than eight data pairs with both results considered detections, then precision and regression analyses were performed; the results are presented in **Table 14-1**. If there were eight or fewer data pairs with both results above the detection limit, the ratios of the individual duplicate sample pairs were averaged; the average, minimum, and maximum ratios for selected analytes are given in **Table 14-2**. The mean ratio should be between 0.7 and 1.3.

Table 14-3. Quality assurance duplicate sampling. Summary statistics for analytes with at least four pairs in which one or both results were below the detection limit.

Medium	Analyte	Number of inconsistent pairs	Number of pairs	Percent of inconsistent pairs
Air	Tritium (air)	1	16	6.3
Ground water	Barium	1	13	7.7
	Beryllium	1	25	4.0
	Chromium	1	7	14.3
	Copper	1	23	4.4
	Gross alpha	2	7	28.6
	Lead	1	26	3.9
	U-235+236	1	12	8.3
Runoff	Carbonate alkalinity (as $CaCO_3$)	2	5	40
	Nitrite (as N)	1	4	25
Sewer	Aluminum	1	4	25
	Arsenic	1	6	16.7
	Cadmium	1	8	12.6
	Chromium	1	4	25
	Gross alpha	2	34	5.9
	Silver	1	6	16.7

If one of the results in a pair is a nondetection, then the other result should be less than two times the detection limit. **Table 14-3** identifies the sample media and analytes for which at least one pair failed this criterion. Analytes with fewer than four pairs total are omitted from the table.

Collocated sample comparisons are more variable when the members of the pair are analyzed by different methods or with different criteria for analytical precision. For example, radiological analyses using different counting times will have different amounts of variability.

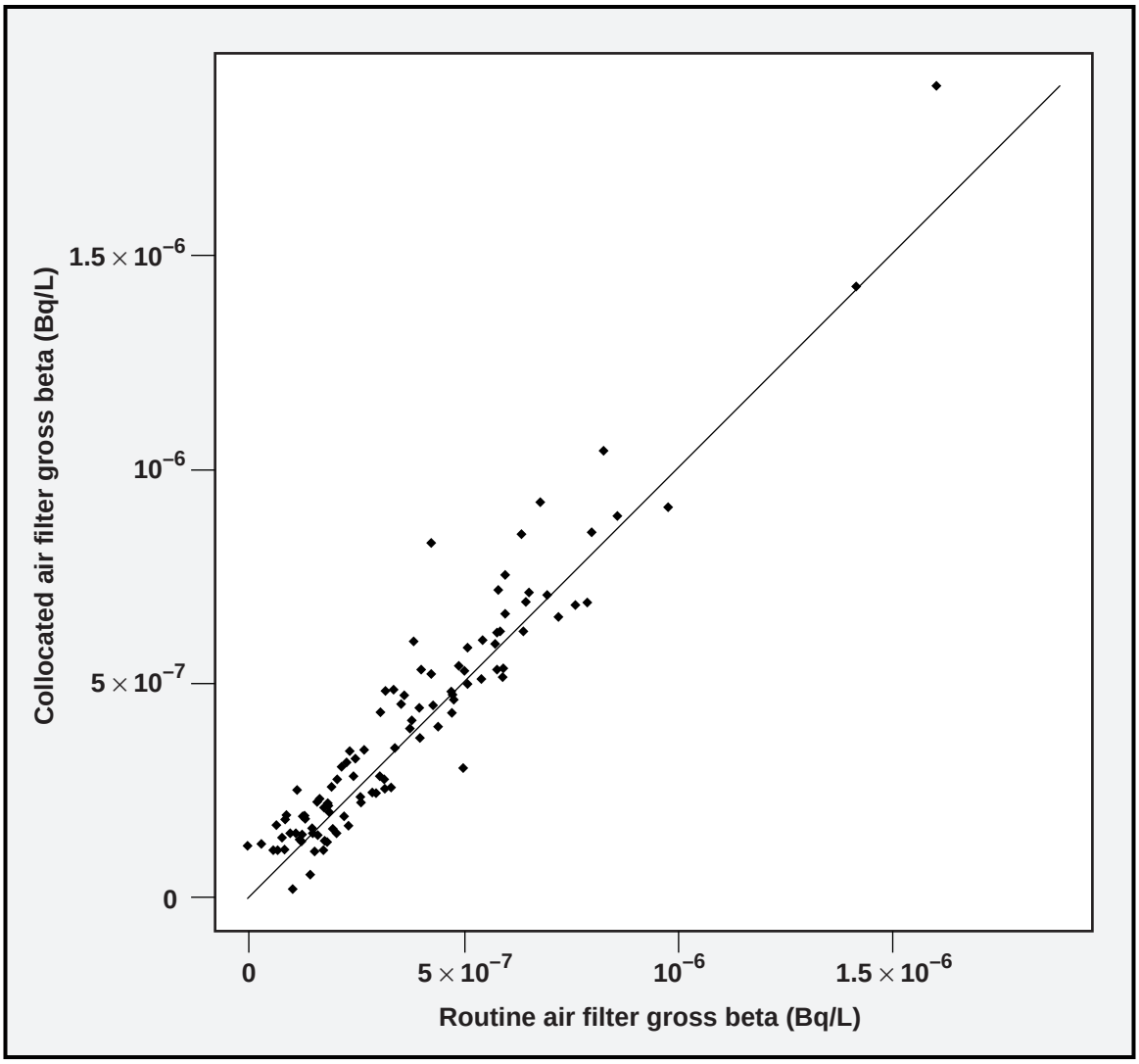

Figure 14-1. Air-filter gross beta concentrations from collocated samples. These data lie close to a line with slope equal to one and intercept equal to zero.

These analyses show generally good agreement between routine samples and quality assurance duplicates: approximately 90% of the pairs have a precision better than 30%. Data sets not meeting our precision criteria generally fall into one of two categories. The first category, outliers, can occur because of data transcription errors, measurement errors, or real but anomalous results. Of 22 data sets reported in **Table 14-1**, 4 did not meet the criterion for acceptability because of outliers. **Figure 14-2** illustrates a set of collocated pairs with two outliers. The other category of results that does not meet the criterion for acceptability consists of data sets in which there is a lot of scatter. This tends to be typical of nondetections and measurements at extremely low concentrations,

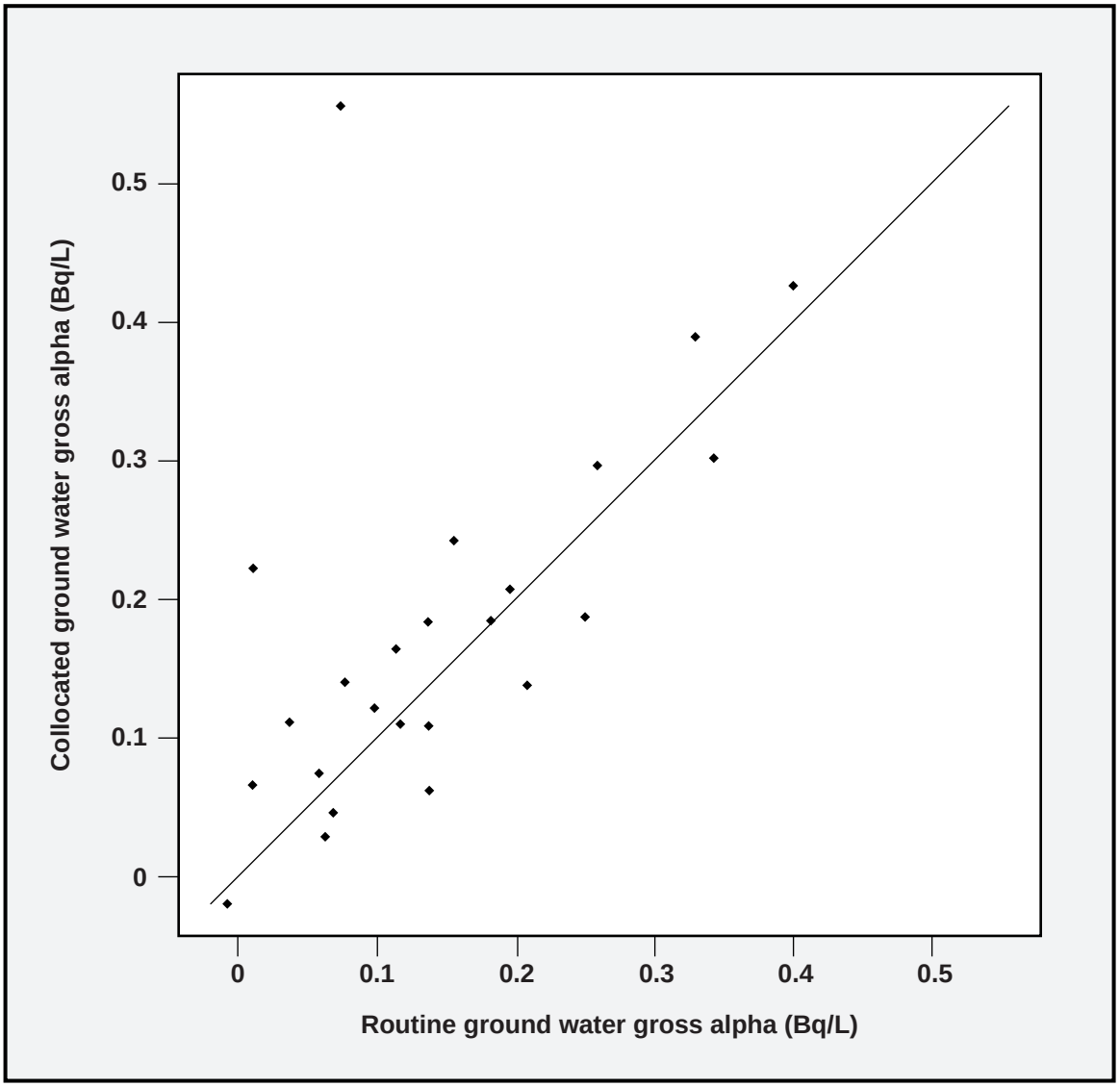

Figure 14-2. Ground water gross alpha concentrations from collocated samples showing two outliers.

as illustrated in **Figure 14-3**. Only three of the data pairs in **Figure 14-3** are above the detection limit, which illustrates why the acceptability criteria apply only to pairs in which both results are detections.

Low concentrations of radionuclides on particulates in air highlight this effect even more because one or two radionuclide-containing particles on an air filter can significantly affect results. Another cause of high variability is sampling and analytical

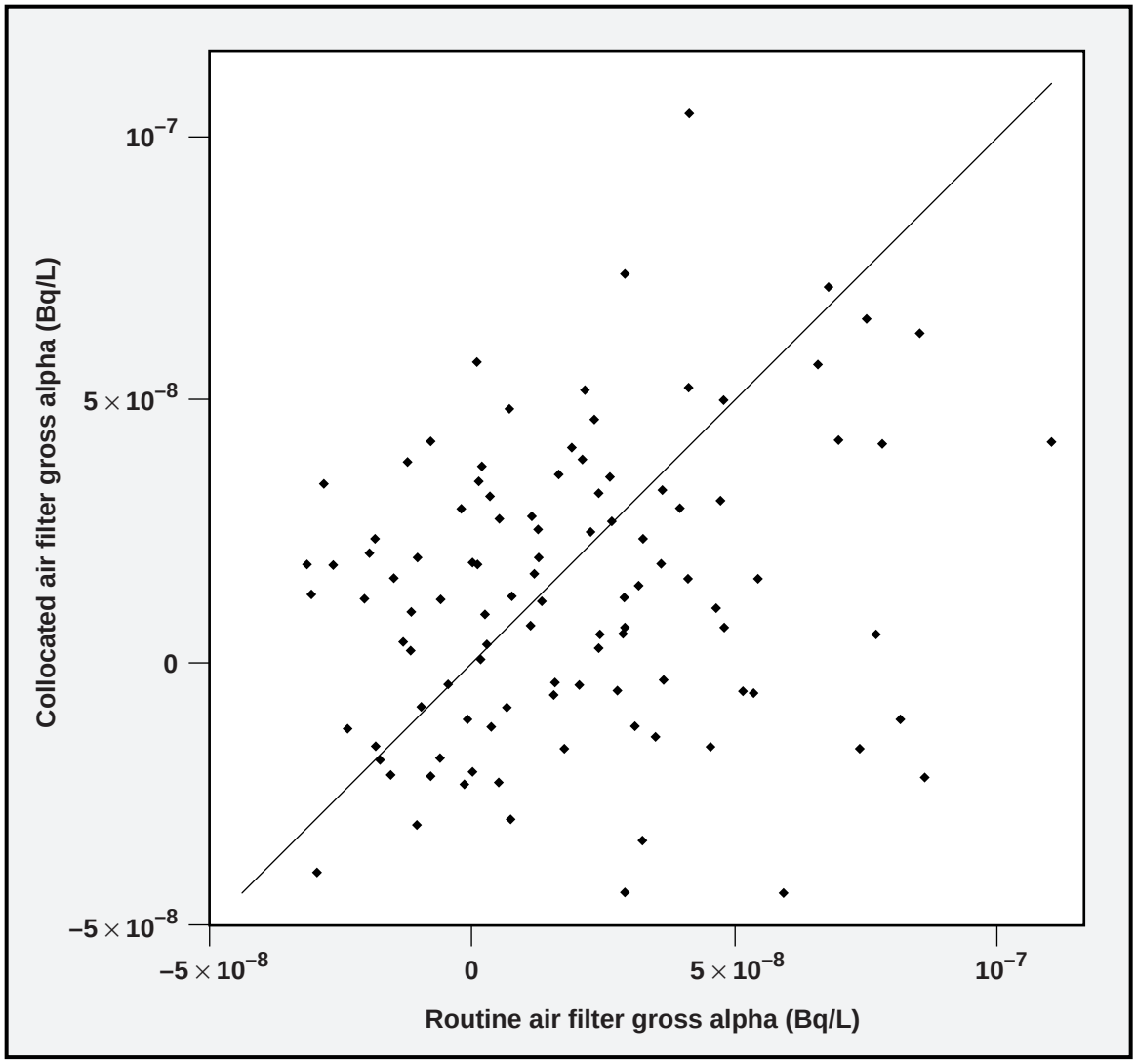

Figure 14-3. Air-filter gross alpha concentrations from collocated samples showing a lot of scatter.

methodology. Analyses of total organic carbon and total organic halides in water are particularly difficult to control. Of the 22 data sets in **Table 14-1**, 2 show sufficient variability in results to make them fall outside of the acceptable range.

Deviations and Changes to the Sampling Program

The sections that follow summarize changes to the environmental sampling effort made during 1998, deviations from planned environmental sampling, and omissions of data expected from regularly scheduled samples.

Changes to Environmental Monitoring Networks

Changes that were made to environmental monitoring networks in 1998 are summarized in **Table 14-4.**

Table 14-4. Changes to environmental monitoring networks in 1998.

Environmental medium	Livermore site	Site 300
Air particulate	Added location L-AMON, 3/98	No changes
Air tritium	Added location L-AMON, 3/98	Added 3-PRIM
Soil	No changes	No changes
Arroyo sediment	No changes	No changes
Vegetation	Sampling frequency for locations L-PIN1 and L-PIN2 changed from monthly to quarterly	No changes
Wine	No changes	Not applicable
Rain	No changes	No changes
Storm water runoff	Minor changes to requested analyses	Minor changes to requested analyses
Drainage retention basin	Minor changes to requested analyses; added suite of samples for dry season releases in second quarter 1998	Not applicable
Other surface water	No changes	Not applicable
Ground water	No changes	No changes
Sewage	No changes	Not applicable
WDR-248 networks	Not applicable	No changes
Thermoluminescent dosimeters (TLDs)	No changes	No changes
Cooling towers	Not applicable	No changes

Sampling Completeness

Planned samples and actual samples collected and analyzed in 1998 are summarized in **Table 14-5**.

Table 14-5. Sampling completeness in 1998, Livermore site and Site 300.

Environmental medium	Number of analyses planned	Number of analyses completed	Completeness (%)	Reason(s) for lost samples
Air particulate (Livermore)				
Radiological parameters	1300	1298	99.8	Equipment problems (1), sample lost at laboratory (1)
Beryllium	96	95	99	Sampler oversight (1)
Air particulate (Site 300)				
Radiological parameters	592	586	99	Equipment problems (3), sample lost at laboratory (1), access to area denied (2)
Beryllium	72	71	99	Sampler oversight (1)
Air tritium				
Livermore	529	509	96	Equipment problems (16), flask broke in transit (4)
Site 300	26	24	92	Equipment problems (2)
Soil				
Livermore	42	42	100	
Site 300	32	32	100	
Arroyo sediment (Livermore only)	54	48	89	Location inundated; could not sample (6)
Vegetation				
Livermore	68	67	99	No vegetation (1)
Site 300	32	32	100	
Wine	22	22	100	
Rain				
Livermore	34	33	94	Sample missing
Site 300	8	6	75	Insufficient rainfall during sample period (2)
Storm water runoff				
Livermore	350	348	96	Sample not submitted for analyses (1); sample lost at laboratory (1)
Site 300	264	153	58	No flow at locations (111)
Drainage Retention Basin				
Field measurements	874	809	93	Sampler error (65)
Samples	126	119	94	Sampler error (7)
Releases	35	35	100	

Table 14-5. Sampling completeness in 1998, Livermore site and Site 300 (concluded).

Environmental medium	Number of analyses planned	Number of analyses completed	Completeness (%)	Reason(s) for lost samples
Other surface water (Livermore only)	58	58	100	
Ground water				
Livermore	662	662	100	
Site 300	2210	2138	96.7	Wells dry or inaccessible, barcard inoperable (72)
Livermore Valley wells	27	24	88.9	Wells not in operation (2), sampler error (1)
Sewage				
B196	910	908	99.8	Sampler error (2)
C196	376	372	99	Equipment error (2), sampler error (2)
LWRP effluent	128	128	100	
Digester sludge	80	78	98	Lost during transport (2)
WDR-96-248				
Surface impoundment wastewater	78	78	100	
Surface impoundment ground water	96	96	100	
Sewage ponds wastewater	42	42	100	
Sewage ponds ground water	72	72	100	
Thermoluminescent dosimeters (TLDs)				
Livermore	180	156	87	Missing (24)
Site 300	76	66	87	Missing (10)
Cooling towers (Site 300 only)	24	24	100	

Statistical Methods

Statistical methods used in this report have been implemented in accordance with the *Environmental Monitoring Plan* (Tate et al. 1995). These methods reduce the large volumes of monitoring data to summary estimates suitable for temporal and spatial comparisons. Attention is given to estimating accuracy, bias, and precision of all data.

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Data review and analyses are conducted in accordance with the *Environmental Monitoring Plan* and the Operations and Regulatory Affairs data analysis procedure. These documents contain detailed information regarding the acceptability of data and the procedures that are followed for the identification, notification, and correction of suspect data.

Radiological Data

The precision of radiological analytical results is displayed in the Data Supplement tables as the 2σ counting uncertainty. The counting uncertainties are not used in summary statistic calculations. Any radiological result exhibiting a 2σ counting uncertainty greater than or equal to 100% is considered to be a nondetection. The reported concentration is derived from the number of sample counts minus the number of background counts. A sample with a low concentration may, therefore, have a negative value; such results are reported in the tables and used in the calculation of summary statistics and statistical comparisons.

Some Data Supplement tables provide radioactivity sensitivity measurements instead of, or in addition to, a reported value when the radiological result is below the detection criterion. These measurements can be described as the smallest concentration of radioactive material that can be detected (distinguished from background) with some specified degree of confidence. These radioactivity sensitivity measurements are referred to as minimum detectable concentration (MDC) in Chapters 4 and 5, limit of sensitivity (LOS) in Chapter 6, and detection limit (DL) in Chapters 7 and 9. The Chemistry and Materials Science Environmental Services Laboratory (CES) calculates these three terms (MDC, LOS, and DL) in the same manner and reports them in units of Bq/kg or pCi/g or Bq/L and pCi/L depending on the sample matrix.

Nonradiological Data

Nonradiological data that are reported as being below the reporting limit also are displayed in the tables with a less-than symbol. The reporting limit values are used in the calculation of summary statistics as explained below.

Statistical Comparisons

Standard comparison techniques (such as regression, t-tests, and analysis of variance) have been used where appropriate to determine the statistical significance of trends or differences between means. All such tests of significance have been performed at the 0.05 level. When such a comparison is made, it is explicitly stated in the text as being "statistically significant" or "not statistically significant." Other uses of the word "significant" in the text do not imply that statistical tests have been performed. These uses instead relate to the concept of practical significance and are based on professional judgment.

Summary Statistics

Determinations of measures of central tendency and associated measures of dispersion are calculated according to the *Environmental Monitoring Plan* (Tate et al. 1995). For data sets not containing values below the detection criterion, the measures of central tendency and dispersion are the median and interquartile range (IQR). The IQR is the range that encompasses the middle 50% of the data set. Radiological data sets that include values less than zero may have an IQR greater than the median.

For data sets with one or more, but fewer than one half, values below the detection criterion, the measure of central tendency is the median. If the values of the detection limits and the number of values below the detection limit permit (determined on a case-by-case basis), dispersion is reported as the IQR. Otherwise, no measure of dispersion is reported. Statistics are calculated using the reported detection limit value for nonradiological data or the reported value for radiological data.

For data sets with one half or more of the values below the detection criterion, the central tendency is reported as less than the median value. Dispersion is not reported.

Radiation Units

Data for 1998 have been reported in Système Internationale (SI) units to conform with standard scientific practices and federal law. Values in the text are reported in becquerels (Bq) and millisieverts (mSv); equivalent values in picocuries (pCi) and millirems (mrem) are given in parentheses.

Quality Assurance Process for the Environmental Report

Unlike the preceding discussion, which focused on standards of accuracy and precision in data acquisition and reporting, a discussion of quality assurance/quality control procedures for a technical publication per se, must deal with how to retain content accuracy through the publication process. Because publication of a large, data-rich document like this site annual environmental report involves many operations and many people, the chances for introducing errors are great. At the same time, ensuring quality is more difficult because a publication is less amenable to the statistical processes used in standard quality assurance methods.

The QA procedure we used concentrated on the tables and figures in the report and enlisted 37 authors, contributors, and technicians to check the accuracy of sections other than those they had authored or contributed to. In 1998, the 91 illustrations and 77 tables in the main volume and the 108 tables in the Data Supplement were checked. Checkers were assigned illustrations and tables and given a copy of each item they were to check along with a quality control form to fill out as they checked the item. Items to be checked included figure captions and table titles for clarity and accuracy, data accuracy and completeness, figure labels and table headings, units, significant figures, and consistency with text. When checking numerical data, checkers randomly selected 10% of the data and compared it to values in the master database. If all 10% agreed with the database, further checking was considered unnecessary. If there was disagreement in the data, the checker compared another 10% of the data with the database values. If more errors were found, the checker had then to verify every piece of data in the table or illustration.

A coordinator guided the process to ensure that forms were tracked and the proper approvals were obtained. Completed quality control forms and the corrected illustrations or tables were returned to the report editors, who were responsible for ensuring that changes, with the agreement of the original contributor, were made. This quality assurance check resulted in nearly 250 data errors or omissions being corrected. Other corrections were made to footnotes, headings, titles in tables, and graph axes, callouts, and captions in figures.